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DIHYDROASCARIDOLE

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DECOMPOSITION OF ASCARIDOLE AND DIHYDROASCARIDOLE

- by -

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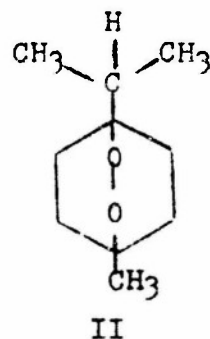
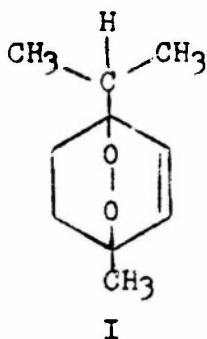
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The kinetics of the decomposition of dihydroascaridole in chlorobenzene, tetralin, and methacrylonitrile at 115° and ascaridole in methacrylonitrile have been studied. In the latter solvent detailed studies have been made of polymerization rate and molecular weight of polymer produced by the thermal decomposition of the two peroxides as well as by di-tert-butyl peroxide. It is concluded that the two cyclic peroxides initiate polymerization via monoradicals, and in the case of dihydroascaridole, the efficiency of initiation is calculated to lie within 55-100%. A mechanism for the decomposition of dihydroascaridole is presented which specifies dismutation of the primary, diradical to a non-cyclic diketone and an excited ethylene molecule. The latter is presumed to initiate monoradical chains in a manner analogous to the thermal initiation of vinyl polymerization.

The decomposition of ascaridole, I, (1,4-epidioxy-2-p-menthane) and dihydroascaridole, II, (1,4-epidioxy-p-menthane) by the action of heat³, light⁴, and metallic ions^{3a,5} has been studied by several workers. The recent work of Russell and Tobolsky⁴ has demonstrated that the primary radicals produced by the photolysis of ascaridole in methyl methacrylate at 60° rapidly react in some uncertain manner to produce

1. This study was initiated under Contract N123s-61517 with the U.S. Naval Ordnance Test Station and completed under Contract N6onr-26309 with the Office of Naval Research.
2. Taken in part from the thesis of R. Zand submitted to the Chemistry Department of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the M.S. degree.
3. (a) E.K. Nelson, *This Journal*, 33, 1404 (1911); (b) O. Wallach, *Ann.*, 392, 52 (1912); (c) F. Richter and W. Presting, *Ber.* 64, 878 (1931); (d) H. Thoms and W. Dobke, *Arch. Pharm.* 268, 128 (1930); (e) C.G. Moore, *J. Chem. Soc.*, 234 (1951).
4. K.E. Russell and A.V. Tobolsky, *This Journal* 76, 395 (1954).
5. H. Paget, *J. Chem. Soc.*, 829 (1938).

monoradical initiation of polymerization. The present investigations support the experimental observations of these workers and enable a somewhat more detailed consideration of the decomposition reaction in the case of dihydroascaridole, consistent with the product analysis reported by Moore^{3e}.



EXPERIMENTAL

Reagents. Methacrylonitrile (Shell Development Co.) was vacuum distilled from inhibitor under nitrogen: b.p. 37.5° (100 mm.), n_D^{20} 1.4007.

Dimethylformamide (Matheson, Coleman and Bell, Inc.) and chlorobenzene (Eastman Kodak Co., b.p. 130-132°.) were used as received.

Tetralin (Fisher Scientific, purified grade) was washed with concentrated sulfuric acid until the washings were colorless and then washed repeatedly with distilled water and stored over anhydrous magnesium sulfate. Prior to use it was distilled under purified nitrogen and the fraction distilling

at 46° (1 mm.) collected. The purified product gave no response to iodometric peroxide tests.

Ascaridole (Burroughs, Wellcome Co.) was used as obtained or was prepared by distillation of chenopodium oil (Amend Drug and Chemical Co.). Ascaridole obtained by distillation from chenopodium oil had a b.p. 65-70° at less than 1 mm., n_D^{30} 1.4709. An infrared absorption spectrum of the product did not differ significantly from that reported by Szmant and Halpern⁶.

Dihydroascaridole was prepared from purified ascaridole according to the method of Paget. After repeated recrystallization, the product exhibited a m.p. 19-19.5°. Tests on aliquots with bromine and potassium permanganate indicated no unsaturation in the compound.

Analytical⁷: calculated for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59

Found: C, 70.69, 70.55 Av. 70.62; H, 10.44, 10.37 Av. 10.41

Di-tert-butyl peroxide 97-98% pure, (Shell Development Co.) was used as obtained.

The reagents employed for iodometric analysis were of the highest available purity and were used as obtained.

6. H. H. Szmant and A. Halpern, This Journal 21, 1133 (1949).

7. Analyses performed by Schwarzkopf Laboratory

Polymerization of Methacrylonitrile. The following procedure was employed in all polymerization runs of methacrylonitrile using ascaridole, dihydroascaridole, or di-t-butyl peroxide as initiator. Into clean Pyrex ampules were placed weighed quantities of peroxide initiator and 10 ml. of freshly distilled monomer, followed by the addition of 5 ml. of dimethyl formamide. The latter solvent was required to prevent the precipitation of polymer during the course of reaction. The Pyrex ampules were degassed, subjected to repeated thawing and freezing operations, and sealed in vacuo of less than 10^{-4} mm. The ampules were immediately placed in an oil bath maintained at $115 \pm 0.5^\circ$. Polymerization times for each system were determined by trial experiment.

On removal from the polymerization bath the ampules were opened and the contents diluted two-fold with acetone. The polymer solutions were then added dropwise to a 10-fold excess of methanol with constant stirring. Polymer was precipitated in the form of finely divided particles and was collected on fritted glass filters. After several washings with methanol, the samples were dried in vacuo at 40° and weighed.

Aliquots of the polymer samples were dissolved in acetone and limiting viscosity numbers determined from viscosity measurements at four concentrations using an Ubbelohde dilution viscometer having a flow time of 124 seconds for

acetone at 20°. At this flow time, kinetic energy corrections are not required. Molecular weight-viscosity data for unfracti-
 onated polymethacrylonitrile terminated by disproportiona-
 tion (transfer) have been reported⁸. These data were employed
 to calculate, by the method of Baysal and Tobolsky⁹, equation
 (1) relating limiting viscosity number $[\eta]$ with number average
 degree of polymerization for polymer chains initiated by a
 monoradical source and terminated by recombination.

$$\bar{P}_n = 3.81 \times 10^3 [\eta]^{0.81} \quad (1)$$

Peroxide Determinations. The decomposition of dihydroascari-
 dole in chlorobenzene, tetralin, and methacrylonitrile-dimethyl-
 formamide solvents at 115° was followed by iodometric analysis.
 Since normal iodometric methods did not yield reproducible
 results, the hydriodic acid method of Vaughan et al.¹⁰ was
 employed. In the runs involving methacrylonitrile, polymer
 formed during reaction obscured the endpoint of the thiosul-
 fate titration, and for this reason, the polymer was separated
 from the solution before performing the iodometric analysis.
 This was achieved by introducing a known quantity of the
 solution dropwise into a measured excess of glacial acetic
 acid, filtering away the precipitate, and titrating an aliquot
 of the filtrate.

8. N. Fuhrman and R. B. Mesrobian, This Journal, in press.

9. B. Baysal and A. V. Tobolsky, J. Polymer Sci., **9**, 171 (1952).

10. F. H. Dickey, J. H. Reley, F. F. Rust, R. S. Tresede and
 W. E. Vaughan, Ind. Eng. Chem., **41**, 1673 (1949).

RESULTS AND DISCUSSION

Rate and molecular weight measurements have been made on the polymerization of methacrylonitrile at 115° initiated thermally, and by ascaridole, dihydroascaridole, and di-*t*-butyl peroxide. The data are summarized in Table I. It is evident from the values in column 4 that in the concentration range of initiator employed, the thermal polymerization rate is negligible compared to the peroxide initiated rates. The following equation has been derived by Tobolsky and co-workers¹¹⁻¹² relating polymerization rate, R_p , and reciprocal number average degree of polymerization, $1/\bar{P}_n$.

$$1/\bar{P}_n = C_{tr,m} + \frac{C_{tr,cat}R_p^2}{K^2[M]^3} + C_{tr,s} \frac{[S]}{[M]} + \frac{A'R_p}{[M]^2} \quad (2)$$

Where $C_{tr,m}$, $C_{tr,cat}$, and $C_{tr,s}$ are transfer constants for the transfer reaction of growing radicals with monomer $[M]$, catalyst $[cat]$, and solvent $[S]$, respectively. The constant A' is related to the specific rate constants for propagation k_p and termination by combination k_{tc} and disproportionation, k_{td} , by the expression:

$$A' = (2k_{td} + k_{tc})/k_p^2 \quad (3)$$

11. D.H.Johnson and A.V.Tobolsky, This Journal 74,938(1952).

12. B.Baysal and A.V.Tobolsky, J.Polymer Sci., 8,529(1952).

TABLE I

POLYMERIZATION OF METHACRYLONITRILE AT 115°C.

CATALYST CONC. MOLE/LITER	MONOMER CONC. MOLE/LITER	TIME HOURS	-dM/dt MOLES/LITER/SEC.	CONVERSION %	\bar{P}_n	$[\eta]$ cm ³ /gm
-	7.95	6	0.26 x 10 ⁻⁵	0.71	8,000	151
THERMAL INITIATED POLYMERIZATION						
ASCARIDOLE INITIATED POLYMERIZATION						
2.3 x 10 ⁻³	7.95	3	1.04 x 10 ⁻⁵	1.41	5,791	126
4.3 x 10 ⁻³	7.95	3	1.47 x 10 ⁻⁵	1.99	4,680	112
9.1 x 10 ⁻³	7.95	3	1.93 x 10 ⁻⁵	2.62	3,940	102
17.1 x 10 ⁻³	7.95	3	2.79 x 10 ⁻⁵	3.78	3,000	87.6
36.3 x 10 ⁻³	7.95	3	3.78 x 10 ⁻⁵	5.14	2,281	75.4
68.3 x 10 ⁻³	7.95	3	5.28 x 10 ⁻⁵	7.18	2,040	70.8
DI-HYDROASCARIDOLE INITIATED POLYMERIZATION						
4.3 x 10 ⁻³	7.95	6	0.59 x 10 ⁻⁵	1.87	4,350	107.6
9.55 x 10 ⁻³	7.95	6	1.05 x 10 ⁻⁵	2.84	6,100	129.9
17.3 x 10 ⁻³	7.95	6	1.05 x 10 ⁻⁵	3.60	4,090	104.0
38.2 x 10 ⁻³	7.95	6	2.02 x 10 ⁻⁵	5.48	3,760	99.2
69.1 x 10 ⁻³	7.95	6	2.62 x 10 ⁻⁵	7.12	3,099	89.2
146.2 x 10 ⁻³	7.95	6	4.11 x 10 ⁻⁵	11.17	2,020	72.4
DI-TERTIARYBUTYL PEROXIDE INITIATED POLYMERIZATION						
0.99 x 10 ⁻³	7.95	3	3.65 x 10 ⁻⁵	4.96	2,543	80.0
1.70 x 10 ⁻³	7.95	3	4.26 x 10 ⁻⁵	5.79	2,380	77.2
4.0 x 10 ⁻³	7.95	3	7.15 x 10 ⁻⁵	9.73	1,319	55.6
6.8 x 10 ⁻³	7.95	3	8.21 x 10 ⁻⁵	11.15	1,140	51.2
15.8 x 10 ⁻³	7.95	3	14.0 x 10 ⁻⁵	18.96	1,683	38.0

The overall rate constant K arises in the rate expression

$$R_p = K [M] [Cat]^{1/2} \quad (4)$$

Values of $1/\bar{P}_n$ are plotted against R_p in Figure 1, as taken from data given in Table I.

It is evident that all experimental points lie on a common straight line. The linearity of the plot indicates that no significant transfer reactions occur between growing polymer radicals and the peroxide initiators, i.e. the second term on the right in equation (2) is zero. The magnitude of the intercept on the ordinate axis in Figure 1 is 0.5×10^{-4} , signifying that the sum of the transfer constants of the methacrylonitrile radical with its monomer and with dimethylformamide solvent is on this order of magnitude. Since the polymerization data obtained with ascoridole and dihydro-ascoridole lie on the same linear plot as those obtained with di-*t*-butyl peroxide, a known monoradical initiator, it is evident that the former two peroxides also initiate via monoradicals.

The rate of initiation of polymer chains, R_i , in methacrylonitrile at 115° by various initiators can be obtained from the relation¹² (assuming no disproportionation)

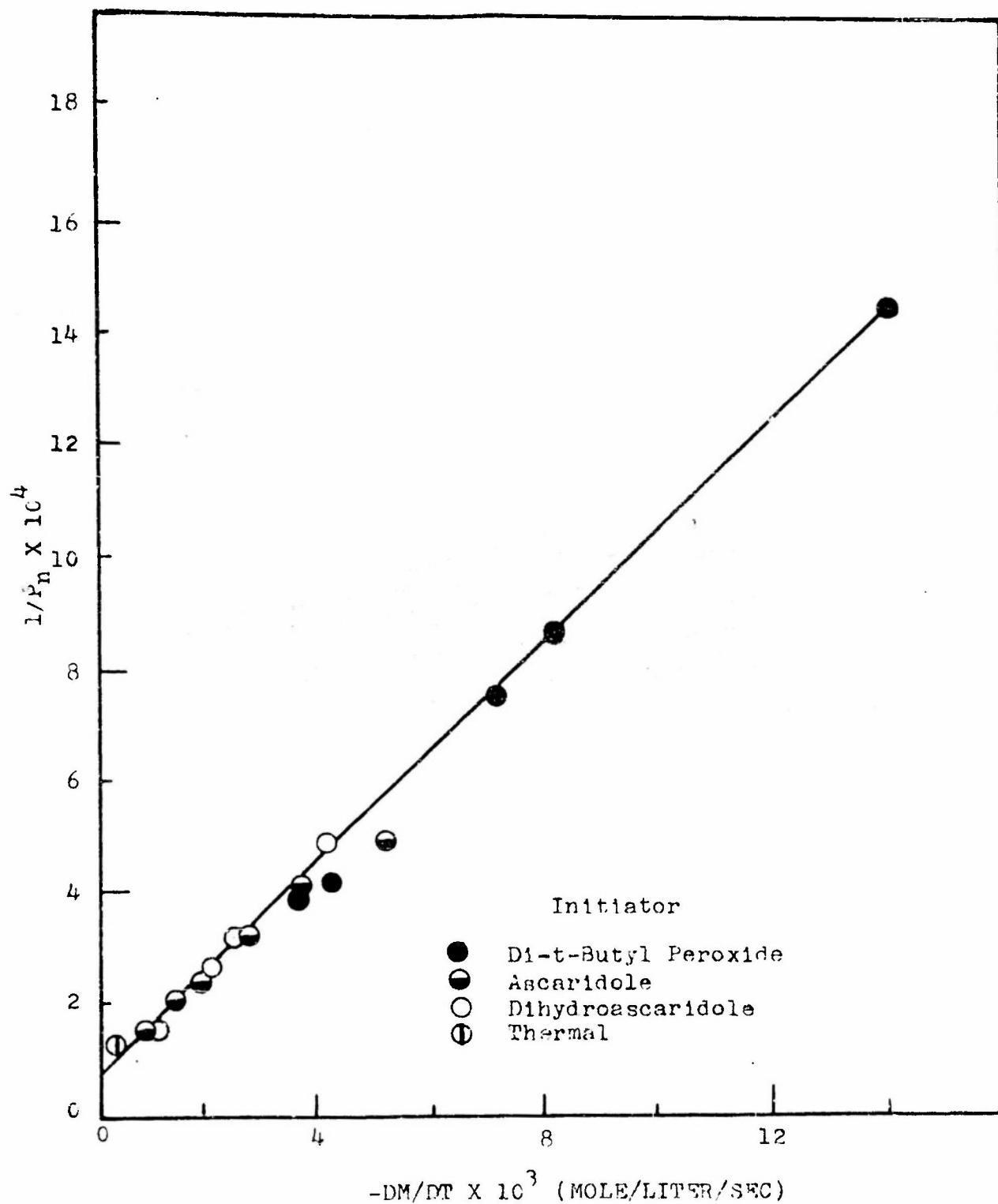
$$R_i = \frac{2A'}{[M]^2} R_p^2 \quad (5)$$

where A' , as defined in equation (2), is calculated from the slope of the line in Figure 1 to be $6.76 \text{ } \ell\text{-sec.-m}^{-2}$.

Figure 1

POLYMERIZATION OF METHACRYLONITRILE AT 115°C.

[M] = 7.93 moles/liter in dimethylformamide



The rate of initiation may also be defined by the relation:

$$R_i = 2fk_d [\text{Cat}] \quad (6)$$

where $k_d [\text{Cat}]$ is the rate of spontaneous, unimolecular decomposition of the catalyst and f , the catalyst efficiency, is the fraction of primary radicals which are effective in starting chains. The rates of decomposition of dihydroascaridole in tetralin, chlorobenzene, and methacrylonitrile-dimethyl formamide at 115° have been followed by iodometric titrations. Table II lists the unimolecular rate constants, k_d , for the decompositions in each of the solvents.

TABLE II.
DECOMPOSITION OF DIHYDROASCARIDOLE AT 115° IN VARIOUS SOLVENTS

Solvent	$k_d^a \times 10^6 \text{ secs.}^{-1}$	Initial Peroxide conc. m/l $\times 10^3$
Tetralin	0.90	23.9
Chlorobenzene	0.72	25.2
Methacrylonitrile- dimethylformamide (10:5 volume ratio)	0.92	24.9

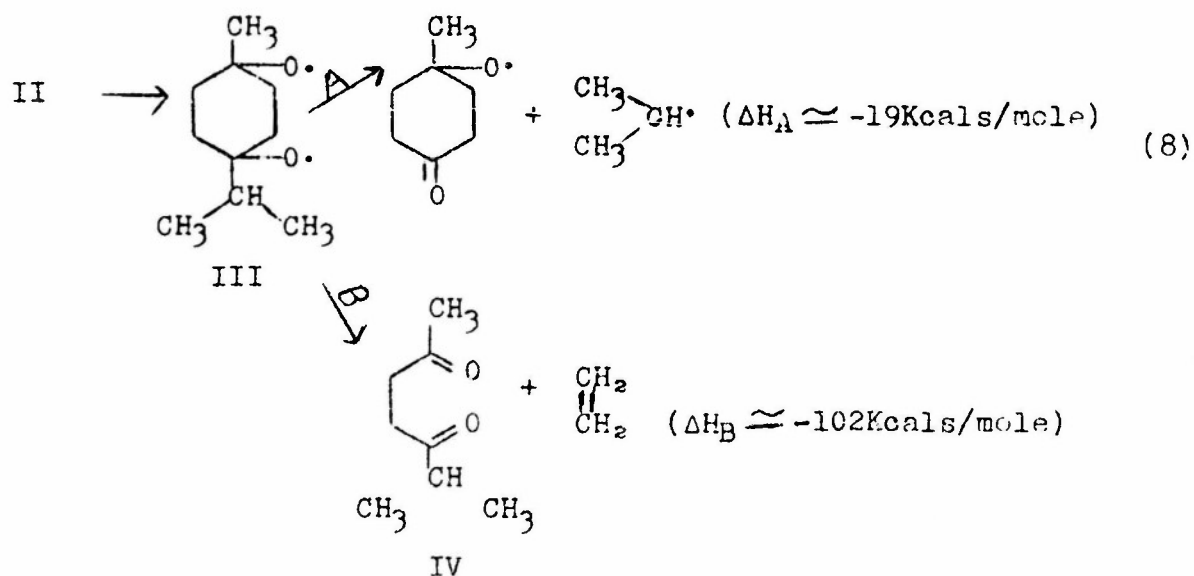
a. The rate constant in each solvent was evaluated from four or more experimental values in the range of 4-19% decomposition.

On combining equations (5) and (6) the catalyst efficiency may be expressed by the relation:

$$f = \frac{2A'}{[M]^2} R_p^2 / 2k_d [\text{Cat}] \quad (7)$$

In the concentration range 4.3 to $146.2 \times 10^{-3} \text{m/l}$ of dihydroascaridole (data of Table I) the average value for f calculated from equation (7) is 1.1 assuming no disproportionation. If termination of growing chains occurs exclusively by disproportionation, f will have the value 0.55 . In either event it is apparent that the majority of the radicals derived by the decomposition of dihydroascaridole initiate polymer chains in the form of monoradicals. Additionally, the observation that k_d (Table II) does not vary appreciably for decompositions run in three widely different solvents, is suggestive that recombination of primary diradicals to reform dihydroascaridole according to the cage principle plays a minor role in this decomposition.

A convenient mechanism to describe the transformation of the primary diradical (III) into a monoradical pair, is that denoted by (A) in equation (8).

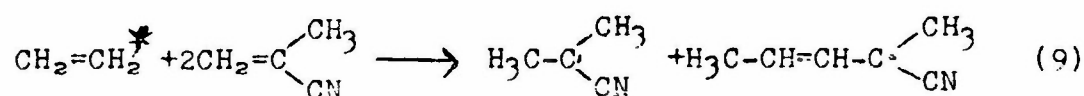


On the other hand Moore¹³ has identified the diketone IV to be one of the major products obtained when pure dihydroascaridole is thermally decomposed at 240°. Other decomposition products were an unidentified gas and a viscous, polymeric residue¹³. The mechanism proposed by Moore to describe the formation of the diketone is denoted by (B) in equation (8). This mechanism specifies that the primary diradicals dismutate to non-radical structures which, in principle, should not initiate vinyl polymerization. An approximate calculation of the heat changes involved in the processes (8A) and (8B) indicates that whereas (8A) is exothermic by 19.2 Kcals., (8B) is considerably more exothermic ($\Delta H_B \approx 102$ Kcals.)¹⁴. Although it cannot be assumed in the absence of experimental data or detailed theoretical calculations that a reaction will follow the energetically more favorable path, since it is known that (8B) predominates at 240° it is probably the preferred path at 115° as well. The ethylene molecule, appearing in mechanism (8B) will undoubtedly contain energy in excess

13. The mole percent of diketone, expressed as moles of product per mole of decomposed dihydroascaridole times 100, is calculated to be 43 and 105 for the gaseous product, assuming it to be ethylene.

14. The heats of reaction are calculated from bond energy values given by M.J.S.Dewar, The Electronic Theory of Organic Chemistry, Oxford Univ. Press, London, p.32, 1949. Resonance energies for the alkoxy and propyl radicals were taken to be zero. The difference in free energy between the two processes (8A) and (8B) is probably even greater than the difference in ΔH since the ring cleavage in (8B) imparts a significant entropy increase.

of the ground state of ethylene. The degree and nature of excitation are unknown but one might reasonably assume the molecule to be excited in its vibrational degrees of freedom. It is realized qualitatively that the required activation energy for a process can be lowered when one of the colliding partners is excited in vibrational energy¹⁵, and accordingly one might picture the reaction of a "hot" ethylene molecule and methacrylonitrile to involve the transfer of a hydrogen atom from one monomer to the other to produce two monoradicals. From detailed studies of the thermal polymerization of styrene, however, Mayo¹⁶ has observed that the initiation process arises from a third-order reaction with monomer to produce monoradicals. Presumably two monomers interact to form an activated complex which on further collision with monomer produces two monoradicals. The analogous process involving an excited ethylene molecule can be represented by equation (9).



It would be of interest to study the polymerization reaction

15. S. Glasstone, K.J.Laidler and H.Eyring, The Theory Of Rate Processes, McGraw-Hill Book Co.Inc., pp.289-295, 1941.

16. F. R. Mayo, This Journal 75, 6133 (1953).

initiated by dihydroascaridole over a wide monomer concentration range. At low monomer concentrations one might expect the polymerization rate to decrease markedly due to energy loss of the excited ethylene molecule by repeated collisions with inert solvent molecules.